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(54) **Title of the Invention:** Epoxy resin composition

(57) Abstract

Problem

To provide an epoxy resin composition that exhibits an excellent adhesiveness for honeycomb while maintaining heat resistance and water resistance.

Solution

An epoxy resin composition comprising

- (a) dicyclopentadiene skeleton-containing epoxy resin,
- (b) glycidylamino-functional aromatic epoxy resin,
- (c) aromatic amine, and
- (d) carboxy-modified acrylonitrile-butadiene rubber and/or carboxy-modified hydrogenated acrylonitrile-butadiene rubber

wherein

the rubber component (d) is present at 5 weight parts to 10 weight parts per 100 weight parts of the epoxy resin.

Claim

Claim 1.

An epoxy resin composition comprising

- (a) dicyclopentadiene skeleton-containing epoxy resin,
- (b) glycidylamino-functional aromatic epoxy resin,
- (c) aromatic amine, and
- (d) carboxy-modified acrylonitrile–butadiene rubber and/or carboxy-modified hydrogenated acrylonitrile–butadiene rubber

wherein

the rubber component (d) is present at 5 weight parts to 10 weight parts per 100 weight parts of the epoxy resin.

Detailed Description of the Invention

[0001]

Technical Field of the Invention

The present invention relates to an epoxy resin composition that maintains heat and water resistance, that exhibits excellent flow control characteristics, and that exhibits excellent adhesiveness for honeycombs. More particularly, the present invention relates to an epoxy resin composition that employs specific epoxy resin and curing agent and that exhibits co-curability with regard to honeycomb/prepreg bonding.

[0002]

Description of the Prior Art

Epoxy resin compositions are used in a variety of fields (construction, civil engineering, automotive, aviation, electrical, and so forth) as highly heat-resistant resins. Examples of these epoxy resins and materials that use them are provided hereafter. For example, Japanese Published (Examined or Kokoku or B) Patent Application Number Hei 7-17732 (17,732/1995) describes an improved flexibility for the matrix resin used in composite materials with carbon fiber. This is achieved by incorporating a curing agent, such as diaminoxylene, in epoxy resin comprising 10 to 90 weight% tricyclodecane ring-containing epoxy resin and 10 to 40 weight% bisphenol-type epoxy resin or novolac-type epoxy resin. Japanese Laid Open (Unexamined or

Kokai or A) Patent Application Number Hei 2-51538 (51,538/1990) describes a composite material afforded by adding large amounts of dicyandiamide and diaminodiphenyl sulfone (DDS) to epoxy resin comprising glycidyl diamino group-containing epoxy resin and other epoxy resin. The resulting composite material exhibits an improved resistance to interlayer separation. Japanese Laid Open (Unexamined or Kokai or A) Patent Application Number Hei 2-14213 (14,213/1990) describes the preparation of a matrix resin for composite materials that exhibit high toughness while maintaining heat resistance. This is achieved by the addition of aromatic diamine to brominated bisphenol A glycidyl ether-type epoxy resin and bisphenol F glycidyl ether-type epoxy resin. Japanese Laid Open (Unexamined or Kokai or A) Patent Application Number Hei 5-239317 (239,317/1993) describes a resin composition afforded by adding solid rubber to an epoxy resin, for example, a bisphenol type, and for which a specific relationship obtains between the viscosity measured at a 0.02 Hz vibration frequency and the viscosity measured at a 2 Hz vibration frequency.

[0003]

However, when these epoxy resins are employed as, for example, resins for preregs that are used in aircraft wherein the flat surface of the prepreg is mated to the honeycomb-patterned surface of a resin honeycomb followed by curing, instances are seen with respect to the use of these prior-art resins in which the resin has an overly low viscosity and ultimately flows out of the prepreg, resulting in inadequate bonding between the prepreg and the honeycomb — leading to the absence of water resistance — and/or resulting in separation of the prepreg from the honeycomb material. In addition, when large amounts of the rubber component are used, dilution with a solvent then becomes necessary for prepreg fabrication, in which case excess solvent remains in the prepreg and can lead to void production. When fabrication in the absence of solvent is attempted, the resulting excessively high viscosity can in some cases make fabrication quite problematic.

[0004]

Problems to Be Solved by the Invention

In order to solve the problems identified above, an object of the present invention is to provide an epoxy resin composition that is a highly heat-resistant, highly water-resistant matrix resin for prepreg applications and that also exhibits an excellent adhesiveness for honeycomb materials.

[0005]

Means Solving the Problems

The inventors carried out extensive and intensive investigations in order to solve the problems identified above and as a result discovered that an epoxy resin composition comprising dicyclopentadiene skeleton-containing epoxy resin, glycidylamino-functional aromatic epoxy resin, curing agent, and acrylonitrile–butadiene rubber and/or hydrogenated acrylonitrile–butadiene rubber and their carboxyl modifications, is an excellent composition that exhibits excellent heat resistance and water resistance when applied as a prepreg matrix resin and that also exhibits satisfactory adhesiveness for honeycombs when applied as a prepreg matrix resin. This invention was achieved based on this discovery.

[0006]

More specifically, the present invention provides an epoxy resin composition comprising

- (a) dicyclopentadiene skeleton-containing epoxy resin,
- (b) glycidylamino-functional aromatic epoxy resin,
- (c) aromatic amine, and
- (d) carboxy-modified acrylonitrile–butadiene rubber and/or carboxy-modified hydrogenated acrylonitrile–butadiene rubber

wherein

the rubber component (d) is present at 5 weight parts to 10 weight parts per 100 weight parts of the epoxy resin.

[0007]

Embodiments of the Invention

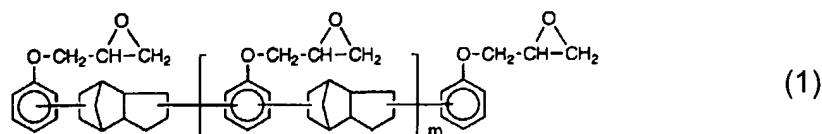
The present invention will be described in detail in the following. The dicyclopentadiene skeleton-containing epoxy resin (a) used by the present invention may be any epoxy resin that contains at least one dicyclopentadiene skeleton within the molecule. A single such epoxy resin may be used, or two or more may be used in combination.

[0008]

The epoxy resin (a) can be exemplified by the tricyclo[5,2,1,0^{2,6}]decane ring-containing epoxy resin with the following structure (1) (referred to hereinbelow as the dicyclopentadiene derivative). These dicyclopentadiene skeleton-containing epoxy resins can be prepared by known methods, for example, in which dicyclopentadiene is polymerized with a cresol species

(e.g., meta-cresol) or a phenol species followed by reaction with epichlorohydrin. More specifically, commercial products such as TACTIX-556 (from Dow Chemical) can be used.

[0009]



(m is an integer from 0 to 15)

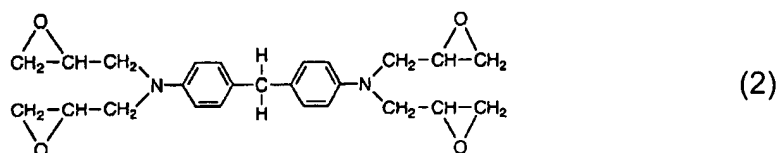
[0010]

The glycidylamino-functional aromatic epoxy resin (b) used by the present invention may be any aromatic epoxy resin that contains at least one glycidylamino group within the molecule, and is not otherwise specifically limited. A single such epoxy resin may be used, or two or more may be used in combination.

[0011]

This epoxy resin (b) can be exemplified by N,N,N',N'-tetraglycidylaminodiphenylmethane with structure (2) below, tetraglycidyl-m-xylylenediamine, triglycidyl-p-aminophenol, N,N-diglycidylaniline, and so forth. These glycidylamino-functional epoxy resins can be synthesized by known methods, for example, by the reaction of epichlorohydrin with a starting amine in the presence of a catalytic amount of water. More specifically, commercial products, such as ELM-434 from Sumitomo Chemical Co., Ltd., or TETRAD-X from Mitsubishi Gas Chemical Co., Inc., can be used.

[0012]



[0013]

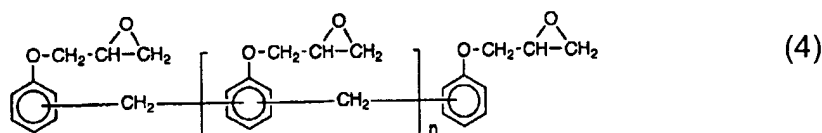
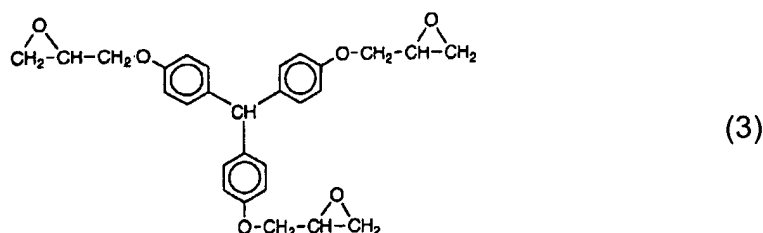
The following proportions are preferred, from the standpoint of striking a balance between the water resistance and heat resistance, for the dicyclopentadiene skeleton-containing epoxy resin (a) and glycidylamino-functional aromatic epoxy resin (b): at least 25 weight% epoxy resin (a) with respect to the total epoxy resin and at least 30 weight% epoxy resin (b) with respect to the total epoxy resin.

[0014]

The sum of the dicyclopentadiene skeleton-containing epoxy resin (a) and glycidylamino-functional aromatic epoxy resin (b) in the total epoxy resin in the epoxy resin composition according to the present invention is at least 55 weight% to less than 85 weight% and preferably 60 to 75 weight%. Values of at least 55 weight% are preferred from the standpoint of the water resistance, while values less than 85 weight% are preferred from the standpoint of the heat resistance. It is difficult to maintain the heat resistance or water resistance when the dicyclopentadiene skeleton-containing epoxy resin (a) or the glycidylamino-functional aromatic epoxy resin (b) is not present in the epoxy resin composition according to the present invention.

[0015]

In addition to the epoxy resin (a) and epoxy resin (b) that are essential components, the epoxy resin composition according to the present invention preferably contains, from the standpoint of obtaining a suitable viscosity and maintaining the heat and water resistance, 15 to 45 weight% and preferably 25 to 40 weight% of another epoxy resin (e) comprising a general-purpose epoxy resin as used in ordinary epoxy resin compositions. This additional epoxy resin (e) can be exemplified by bisphenol A-type epoxy resins, triphenylmethane-type epoxy resins, novolac-type epoxy resins, bisphenol AD-type epoxy resins, and bisphenol F-type epoxy resins. A single such epoxy resin may be used, or two or more may be used in combination. This epoxy resin can be exemplified by glycidyl ether-type epoxy resins with the following structures (3) and (4).

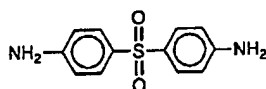


More specifically, commercial products, such as TACTIX-742 from Dow Chemical and EP-154 from Yuka Shell Chemical Co., Ltd., can be used.

[0016]

The aromatic amine (c) used by the present invention must contain diaminodiphenyl sulfone (DDS) from the standpoint of providing heat resistance. The aromatic amine (c) may be a mixture of diaminodiphenyl sulfone (DDS), with structure (5) below, and another aromatic amine. DDS constitutes at least 50% of the total amine and more preferably at least 80%. The other aromatic amine is an aromatic amine that can be used as a curing agent for epoxy resins, but is not otherwise limited. Specific examples are diaminodiphenylmethane (DDM), diaminodiphenyl ether (DPE), and bisaniline, and a single such species can be used or these can be used in mixtures of two or more. A curing agent other than the aromatic amine (c), for example, dicyandiamide (DICY), 3-(3,4-dichlorophenyl)-1,1-dimethylurea (DCMU-99), or an imidazole compound, may be used in combination with the aromatic amine (c). The reason for this is to adjust the cure rate.

[0017]



(5)

[0018]

The content of the aromatic amine (c) used in the present invention preferably gives, from the standpoint of generating heat resistance, an equivalents ratio with the epoxy resin of active hydrogen equivalents from the aromatic amine/epoxy equivalents = 0.6 to 1.2 and particularly 0.7 to 1.0.

[0019]

The rubber component (d) used by the present invention is carboxy-modified acrylonitrile-butadiene rubber and/or carboxy-modified hydrogenated acrylonitrile-butadiene rubber (d) (denoted below as carboxy-modified (hydrogenated) acrylonitrile-butadiene rubber) that contains a functional group capable of reacting with the epoxy resin or curing agent, particularly the carboxyl group. The rubber component (d) can use either the non-hydrogenated species or the hydrogenated species or both the non-hydrogenated species and the hydrogenated species, but the use of the hydrogenated species provides the composition with good resistance to water-induced deterioration, heat, and weathering. The carboxy-modified species can readily react with the epoxy resin or the curing agent due to the presence of the carboxyl group. The invention can use a single carboxy-modified (hydrogenated) acrylonitrile-butadiene rubber (d) or a mixture of carboxy-modified (hydrogenated) acrylonitrile-butadiene rubbers (d). The carboxy-modified (hydrogenated)

acrylonitrile–butadiene rubber preferably has a nitrile content of 20 weight% to 40 weight% and a carboxyl content of 0.5 weight% to 6 weight%. Compositions were prepared by kneading, at the proportions given in Example 1, *infra*, the epoxy resins ((a) + (b) + (e)) used in Example 1 and the acrylonitrile–butadiene rubbers (d) with different carboxyl and nitrile contents that are reported in Table 2, and these compositions were visually evaluated for compatibility. The results are reported in Figure 1. Letting x = the carboxyl content (weight%) and y = the nitrile content (weight%) in Figure 1, then the combinations of carboxyl and nitrile contents bounded by the range defined by $y \geq -1.3x + 35$, $0.5 \leq x \leq 6$, and $25 \leq y \leq 40$ are particularly preferred. In addition, the compatibility declines sharply according to the curve in Figure 1 at a carboxyl content less than 0.5 weight%.

[0020]

The content of the carboxy-modified (hydrogenated) acrylonitrile–butadiene rubber (d) is 5 weight parts to 10 weight parts and preferably 5 to 8 weight parts per 100 weight parts of the epoxy resin in the epoxy resin composition according to the present invention. As shown in Figure 2 (discussed below), the minimum viscosity during cure will be too low and the composition will be prone to sagging when the content of the carboxy-modified (hydrogenated) acrylonitrile–butadiene rubber is less than 5 weight parts per 100 weight parts of the epoxy resin. At above 10 weight parts the viscosity becomes impractically high.

[0021]

While the epoxy resin composition according to the present invention contains epoxy resin (a), epoxy resin (b), aromatic amine (c), and carboxy-modified (hydrogenated) acrylonitrile–butadiene rubber (d) as essential components, it may as necessary additionally contain, within a range that does not impair cure according to the present invention, epoxy resin (e) other than those described above as well as various additives such as other curing agent, imidazole compound, filler, ageing inhibitor, solvent, and so forth.

[0022]

The filler can be exemplified by carbon black, calcium carbonate, titanium oxide, silica, and aluminum hydroxide. The ageing inhibitor can be exemplified by hindered amines, hindered phenols, and so forth. The solvent can be exemplified by methanol, ethanol, propanol, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), and so forth.

[0023]

The epoxy resin composition according to the present invention is prepared by intermixing a

base and curing agent — comprising the starting epoxy resins (a) and (b), aromatic amine (c), carboxy-modified (hydrogenated) acrylonitrile–butadiene rubber (d), and any optional filler, etc. — by a standard method using, for example, a Dalton mixer, paint roll, or kneader. Mixing of the (hydrogenated) acrylonitrile–butadiene rubber in particular may be carried out with dissolution in solvent or using a paint roll, but in any case a thorough dispersion in the epoxy resin must be achieved.

[0024]

In order to investigate the minimum viscosity during cure, compositions were prepared, using the conditions given for the examples in Table 1 below, by varying the content of the carboxy-modified (hydrogenated) acrylonitrile–butadiene rubber (d) from 3 weight parts to 15 weight parts per 100 weight parts epoxy resin ((a) + (b) + (c)). The viscosity during cure was measured on the resulting compositions and is reported in Figure 2. Figure 2 shows the relationship between viscosity and the content of the carboxy-modified (hydrogenated) acrylonitrile–butadiene rubber for epoxy resin compositions containing the carboxy-modified (hydrogenated) acrylonitrile–butadiene rubber (d). It is shown that, when the carboxy-modified (hydrogenated) acrylonitrile–butadiene rubber (d) is present at or above a certain constant value, the compositions exhibit a suitable minimum viscosity that results in an improved water resistance and an improved fillet formability during bonding. Epoxy resin compositions according to the present invention obtained as described preferably have a minimum viscosity, when mixed at the time of use, of 10 to 1000 poise and particularly 70 to 300 poise.

[0025]

The resulting cured product, in addition to heat resistance and water resistance, exhibits an excellent prepreg-to-honeycomb adhesiveness, and the epoxy resin composition according to the present invention is therefore useful, inter alia, as a matrix resin composition for prepreg and as an adhesive.

[0026]

An example of the use of the inventive epoxy resin composition as the matrix resin composition for prepreg is described in the following. Prepreg according to the present invention is fabricated by impregnating the inventive epoxy resin composition into a woven fiber fabric of, for example, carbon fiber, aramid fiber (e.g., Kevlar), or glass fiber, or into these fibers laid out monodirectionally, or is fabricated by stacking a plurality of the resin-impregnated woven fabrics. This impregnation step can employ a wet method that uses solvent or a solventless hot melt procedure. In the case of prepreg fabrication by a wet

method, the epoxy resin composition according to the present invention is dissolved in solvent to prepare a varnish that is then used for impregnation. The solvent used for varnish preparation is preferably an alcohol (e.g., methanol, ethanol, propanol) or a ketone (e.g., methyl ethyl ketone (MEK)). The woven fabric may be impregnated after the epoxy resin composition according to the present invention has been dissolved in such a solvent to prepare a varnish. The solvent is added at 100 to 200 weight parts per 100 weight parts epoxy resin composition, wherein the drying process after fabrication is preferably optimized.

[0027]

The woven fiber fabric used in prepreg in which the matrix resin is the inventive composition is exemplified by woven fiber fabrics of, for example, carbon fiber, aramid fiber (e.g., Kevlar), and glass fiber, and by these fibers (long fibers) laid out monodirectionally. Specific examples are T-300 carbon fiber from Toray Industries, Inc., and HTA Grade carbon fiber from Toho Rayon Co., Ltd. The fiber areal weight is preferably 140 to 200 g/m². Prepreg in which the matrix resin is the inventive composition is preferably prepreg fabricated by impregnating a woven fabric of carbon fiber with the hereinabove-described inventive epoxy resin using a solvent (e.g., varnish) or without solvent. Such prepreg can be fabricated using an apparatus such as a UD (unidirectional) machine. The content of impregnated epoxy resin composition is preferably 30 to 50 weight% in the prepreg and particularly 35 to 45 weight% in the prepreg.

[0028]

The inventive composition can also function as an adhesive for honeycomb in combination with functioning as a matrix resin for prepreg. Use of this prepreg as such also makes it possible to omit the use of a separate adhesive between the prepreg and honeycomb. With regard to the material of the honeycomb, honeycomb with any composition may be used as long as the honeycomb is made of a material, e.g., resin, paper, yarn, or fiber, other than metal. For example, Nomex honeycomb, as afforded by impregnating phenolic resin into Nomex, is most preferred when considering aircraft applications. Various sizes can be used for the hexagonal columns of the honeycomb structure of the honeycomb; however, values of 1/8- to 3/8-inch for the length of the honeycomb cell size are preferred from the standpoints of weight reduction and strength.

[0029]

This means that, when prepreg has been produced using a composition according to the present invention, curing of the prepreg itself can be carried out simultaneously with bonding to honeycomb, that is, so-called co-cure molding can be carried out. Figures 5 and 6 show

examples of structures in which a prepreg has been bonded to a honeycomb and describe a procedure for bonding prepreg to honeycomb. Figure 5 is an oblique drawing of a structure **1**. Figure 6 is a cross-sectional drawing in which the structure **1** has been sectioned in parallel to the sides of the polygons in a honeycomb **11**. The **a** section in Figure 6 shows a structure that uses prepreg made using a prior-art matrix resin, while the **b** section shows a structure that uses prepreg in which the matrix resin is epoxy resin composition according to the present invention. As shown in Figure 5, structure **1** is obtained by bonding a prepreg **10** to a honeycomb **11**, wherein the prepreg **10**, in which the matrix resin is the composition according to the present invention, is mated to the end surface at one or both of the honeycomb-patterned ends **12** of the honeycomb and fabrication is effected by heating and curing in, for example, an autoclave, while pressing from both ends.

[0030]

However, during heating and curing — and even when uniform pressing is applied to the prepreg **10** and the honeycomb **11** —, in some instances when a prior-art composition is used, as shown for the **a** section in Figure 6, the epoxy resin composition drips completely down to the lower surface **13'** while at the upper surface **13** a fillet is not formed and/or gaps are produced in sections of the prepreg **10**/honeycomb **11** bonding plane. In contrast to this, and as shown in the **b** section in Figure 6, in the case of the inventive composition a suitable viscosity is imparted to the epoxy resin composition through the incorporation of the carboxy-modified (hydrogenated) acrylonitrile–butadiene rubber (d), resulting in the formation of a good-quality fillet **14**. Due to this, while honeycomb/prepreg bonding has been incomplete in the prior art, the inventive composition provides complete bonding due to the occurrence of a suitable viscosity range and also avoids excessive outflow of the epoxy resin composition from the prepreg and eliminates the loss of resin component from the prepreg, thereby making it possible for the epoxy resin composition to be present in the prepreg in appropriate amounts. Accordingly, curing can be completed while maintaining a suitable shape for the fillet **14**. When, at the lower surface, the viscosity also undergoes a temporary drop, the fillet **14'** is formed due to surface tension and curing can be completed with the composition being retained to a suitable degree. This fillet denotes the shape of the resin layer formed between the prepreg and honeycomb when the prepreg and honeycomb are mated and curing is carried out (**14** and **14'** in Figure 2).

[0031]

Since the viscosity of the epoxy resin composition according to the present invention can be controlled well enough to enable co-curing, a structure according to the present invention does

not suffer from a loss of the heat resistance of the epoxy resin, has an excellent water resistance that is better than in the prior art, and exhibits excellent prepreg/honeycomb bonding.

[0032]

The following procedure, for example, is preferred with respect to the curing conditions during honeycomb/prepreg bonding: temperature ramp up at 2-5°C/minute to 150-185°C at a pressure of 2.5-4.0 kg/cm²; holding for 1-2 hours at 150-185°C; cool down to room temperature at 2-5°C/minute. The resulting prepreg/honeycomb structure has an excellent heat resistance and water resistance and also exhibits satisfactory prepreg/honeycomb bonding, and for these reasons is useful as a member in, for example, aircraft and automobiles.

[0033]

Examples

The present invention is described in specific detail hereinbelow through examples, but the invention is not limited to these examples.

[0034]

Examples 1 to 7 and Comparative Examples 1 to 9

(1) The epoxy resin compositions

The individual epoxy resin compositions were prepared by mixing the starting components in the proportions reported in Table 1 below; a paint roll was also used in some cases.

[0035]

(2) Evaluations

Each of the epoxy resin compositions prepared in accordance with (1) was subjected to the following evaluations; the results are reported in Table 1 below. Separately, compositions prepared in the examples and comparative examples were submitted to measurement of the glass-transition temperature (T_g) after water-resistance testing; these results are reported, respectively, in Figures 3 and 4 as a function of the nitrile and carboxyl contents.

[0036]

(i) Viscosity

The minimum viscosity during composition cure was measured for each composition using a dynamic mechanical analyzer (DMA) in the parallel plate configuration (plate diameter = 50 mm) at a rate of temperature rise of 2°C/minute and a frequency of 10 rad/second.

[0037]

(ii) Glass-transition temperature (T_g)

Using the same conditions as for honeycomb/prepreg bonding, cured product was prepared from each composition by raising the temperature at 2°C/minute and curing for 2 hours at 180°C. A 5 × 5 × 15 mm bar-shaped sample was cut from the cured product and was submitted to measurement with a thermomechanical analyzer (TMA) using a penetration procedure at a rate of temperature rise of 10°C/minute and a load of 100 g. The inflection point in the resulting curve is reported as T_g .

[0038]

(iii) Glass-transition temperature (T_g) after water resistance testing

Cured product was prepared by curing for 2 hours at 180°C and was immersed for 14 days in hot water (93°C). Upon withdrawal, the sample was immediately submitted to measurement of the glass-transition temperature (T_g) by TMA using a penetration procedure (measurement conditions as above). A glass-transition temperature less than 165°C according to this measurement procedure indicates unsuitability for use after water resistance testing.

[0039]

(iv) Prepreg moldability

A carbon prepreg was fabricated by impregnating 38% of a composition as reported in Table 1 into carbon fiber (T-300 from Toray Industries, Inc., fiber areal weight = 140 g/m²) using a UD machine from The Yokoyama Rubber Co., Ltd. A score of "O" was rendered when the prepreg could be fabricated without problems with the flow and impregnation characteristics of the composition at the machine; a score of "x" was rendered when the viscosity was high and impregnation could not be carried out.

[0040]

(v) Fillet formability

Prepreg fabricated in accordance with (iv) was mated onto Nomex honeycomb (Showa Aircraft Industry Co., Ltd.) on both of the surfaces that presented the honeycomb pattern. The temperature was raised to 180°C in an autoclave at a rate of temperature rise of 2°C/minute while applying a molding pressure of 3 kg/cm² and the test specimen was obtained by holding at 180°C for 2 hours. The resulting test specimen was sectioned in parallel to the polygonal columns of the honeycomb: a score of "O" was rendered when a fillet of at least 200 μm was formed at both the upper and lower ends of the honeycomb; a score of "x" was rendered either when a fillet was not formed or when there was a fillet only on the lower surface. The results are reported in Table 1 below.

[0041]

Table 1.

	examples							comparative examples								
	1	2	3	4	5	6	7	1	2	3	4	5	6	7	8	9
<u>epoxy resin</u>																
(b) glycidylamine type ELM-434	50	50	50	50	50	40	55	50	50	50	50	—	50	50	50	50
(a) dicyclopentadiene type TACTIX-556	25	25	25	25	25	25	30	25	25	25	25	25	25	25	25	25
(e) other epoxy TACTIX-742	20	20	20	20	20	22	20	20	20	20	20	20	20	20	20	20
EP-154	5	5	5	5	5	13	5	5	5	5	5	5	5	5	5	5
ELA-128												50				
<u>curing agent</u>																
DDS	31	31	31	31	31	31	31	31	31	31	31	31	31	31	31	31
DICY	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
DCMU-99	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
<u>acrylonitrile-butadiene rubber</u>																
Zetpol 1072	10	10		5			7				no	10	3		15	
DN631						7					addi-			3		15
Zetpol 2220			10		5			10	10	10	tion					
Zetpol DN101																
Zetpol 1020										10						
Zetpol 0020																
<u>Evaluation results</u>																
T _g	200	190	183	201	196	200	198	192	208	190	220	180	201	200	190	192
T _g after water resistance testing	184	181	170	185	175	175	180	160	164	155	197	150	190	192	163	164
minimum viscosity (poise) of the resin	70	25	30	11	12	27	35	25	60	28	5	100	5	5	110	105
pregreg moldability	○	○	○	○	○	○	○	○	○	○	×	○	×	×	○	○
fillet formability	○	○	○	○	○	○	○	○	○	○	×	○	×	×	○	○

[0042]

Notes to the Table.

The amount of each component is reported in weight parts. The epoxy resins and curing agents referenced in the table are as follows.

ELM-434: glycidylamine-type epoxy resin with formula (2), supra, from Sumitomo Chemical (epoxy equivalent weight = 120)

TACTIX-556: dicyclopentadiene-type epoxy resin with formula (2) [sic], supra, from Dow Chemical (epoxy equivalent weight = 230)

TACTIX-742: triphenylmethane triglycidyl ether (epoxy equivalent weight = 160) from Dow Chemical

EP-154: phenol novolac-type epoxy resin (epoxy equivalent weight = 180) from Yuka Shell Chemical

ELA-128: bisphenol-type epoxy resin (epoxy equivalent weight = 190) from Sumitomo Chemical

DDS: 4,4'-diaminodiphenyl sulfone from Sumitomo Chemical

DICY: dicyandiamide from Yuka Shell Chemical

DCMU-99: 3-(3,4-dichlorophenyl)-1,1-dimethylurea from Hodogaya Chemical Co., Ltd.

[0043]

The carboxy-modified (hydrogenated) acrylonitrile-butadiene rubbers reported in the table are as follows.

Table 2.

			nitrile content (weight%)	carboxyl content (weight%)
carboxy-modified	acrylonitrile-butadiene rubber	Zetpol 1072	27%	5%
		DN-631	33%	0.5%
	hydrogenated acrylonitrile-butadiene rubber	Zetpol 2220	33%	3%
unmodified	acrylonitrile-butadiene rubber	Zetpol DN101	42%	0%
	hydrogenated acrylonitrile-butadiene rubber	Zetpol 1020	44%	0%
		Zetpol 0020	49%	0%

[0044]

Advantageous Effects of the Invention

The epoxy resin composition according to the present invention, while maintaining the heat resistance and water resistance of the resin, enables control to a suitable viscosity during cure. In addition, the epoxy resin composition according to the present invention, because it exhibits excellent prepreg/honeycomb bonding and, when used as a matrix resin for prepreg, can be controlled to a viscosity that forms a good-quality fillet with honeycomb, is useful in particular as a matrix resin composition for prepreg that will be bonded to honeycomb. The epoxy resin composition according to the present invention can endow the prepreg with co-curability and provides viscosity controllability.

Brief Description of the Drawings

Figure 1 is a graph that shows the range, when the carboxyl and nitrile contents in the acrylonitrile–butadiene rubber are varied, of the carboxyl and nitrile contents that exhibit compatibility with epoxy resin.

Figure 2 is a graph that shows the relationship between viscosity and the carboxy-modified (hydrogenated) acrylonitrile–butadiene rubber content (weight parts) in the epoxy resin composition, per 100 weight parts epoxy resin in the epoxy resin composition.

Figure 3 is a graph that shows the relationship between the glass-transition temperature of the epoxy resin composition after water resistance testing and the nitrile content of the carboxy-modified (hydrogenated) acrylonitrile–butadiene rubber present in the epoxy resin composition (content: 10 weight parts rubber content per 100 weight parts epoxy resin).

Figure 4 is a graph that shows the relationship between the glass-transition temperature of the epoxy resin composition after water resistance testing and the carboxyl content of the carboxy-modified (hydrogenated) acrylonitrile–butadiene rubber present in the epoxy resin composition (content: 10 weight parts rubber content per 100 weight parts epoxy resin).

Figure 5 is an oblique diagram of a structure comprising a honeycomb and prepreg.

Figure 6 is a cross-sectional diagram of a structure comprising a honeycomb and prepreg.

Reference Symbols

1	structure
10	pregreg
11	honeycomb
12	end
13	upper surface
13'	lower surface
14	upper fillet
14'	lower fillet
a	structure that uses pregreg formed with prior-art matrix resin
b	structure that uses pregreg in which composition according to the present invention is the matrix resin
c	cell size

Figure 1.

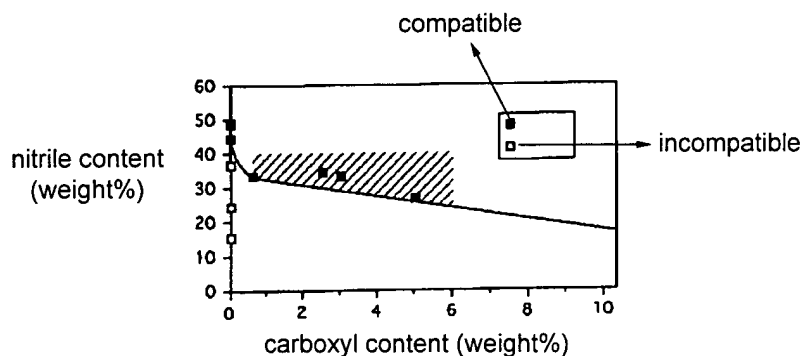


Figure 2.

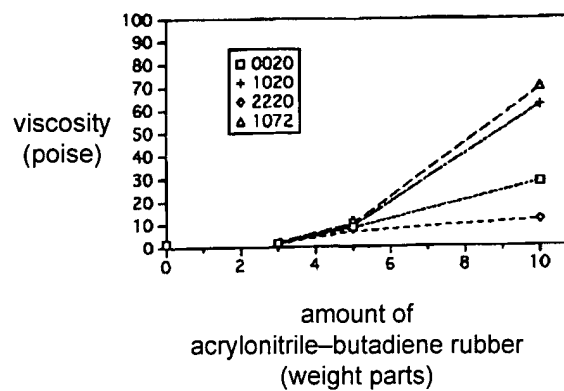


Figure 3.

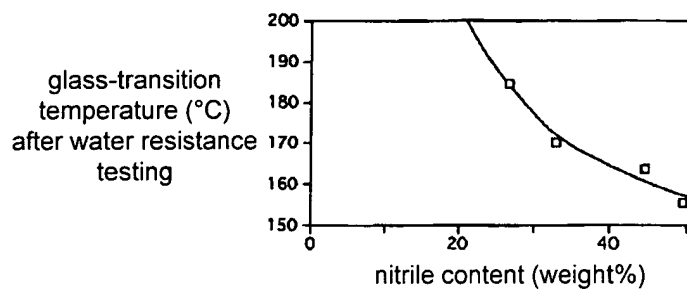


Figure 4.

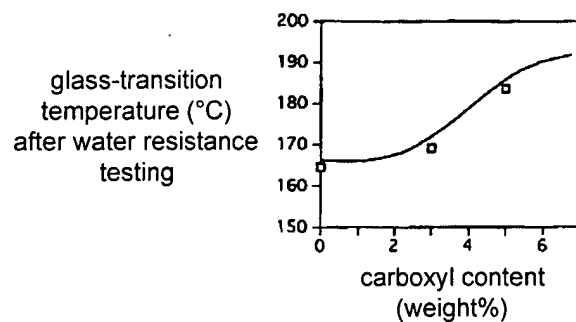


Figure 5.

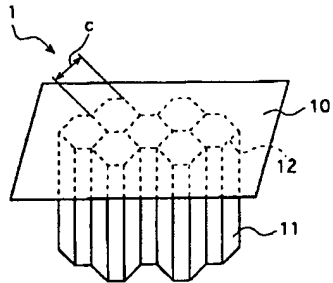


Figure 6.

